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CALCULATION OF THERMODYNAMIC FUNCTIONS OF CHEMICALLY REACTIVE GASES

V. B. Nesterenko and V. P. Bubnov

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Thermodynamic analysis of the dissociating system N_2O_4. The physicochemical properties of N_2O_4 are determined and the entropy and enthalpy are calculated as functions of temperature and pressure. The calculated values are shown to be sufficiently accurate for use in preliminary design of turbines, heat exchangers, and thermodynamic cycles.

The development of energetics, the growth of turbopower units and the /5* creation of small energy plants have pushed into the fore, from out of a whole group of problems, a search for new working substances. The authors believe that one of the paths toward solving this problem is the application of chemically reactive (dissociative) gases as the working substance in a turbine.

The idea of utilizing dissociative gases as the working substance in turbomachinery was at first stated by M. Lighthill [1] in 1957.

The uniqueness of dissociative gases is due to the property of complex molecules of gas to dissociate (decompose) into more simple (with smaller atomic weight) molecules and, therefore, to have a higher gas constant during heating and to recombine into the initial forms upon cooling. This quality of dissociative gases is utilized in the thermodynamic cycle insofar as the work of a turbine and compressor are proportional to the gas constant.

The change (increase) the the gas constant in a turbine permits changing the ratio of useful power to input power of the compressor by 70-75% in conventional gas turbines using inert gases and up to 40-50% in conventional gas turbines using a dissociative gas. As a result of this, the efficiency of gas turbines using a dissociative gas can be made much higher than conventional inert gas turbines. After all, the application of the gas-fluid cycle, proposed by the Institute of Nuclear Electric Power of the Academy of Sciences, BSSR, allows us to get an efficiency in the installation of 40-50% at temperatures of 673-1023° K and at pressures of 60-130 atm.

The application of a dissociative gas also favorably affects the intensification of the heating system, since the heating of the gas is accompanied by greater absorbtion of heat during dissociation.

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*Numbers in the margin indicate pagination in the original foreign text.

The effective properties of a uniform dissociative gas. In the kinetics of chemical reactions, two concepts are accepted; uniform flow and stagnation flow. In uniform flow, the speeds of dissociation and recombination are so great that the change in the chemical composition of the gas system is non-inertial, and practically follows instantaneously the changes in temperature and pressure. In stagnation flow, the rate of chemical reactions are so low that with changes in temperature and pressure, the composition of the gas mixture does not change.

In the theory of mass transfer [2-4], chemical thermodynamics [5-7] and the thermodynamics of irreversible processes [8], it was shown that uniform thermophysical properties are determined by a near combination of two additive constituents. The first is related to the "stagnation" state of the system (inert nonreactive mixture) and the second, the "reactive" constituent. The latter takes into account the effect of heat of chemical reactions on the thermophysical and thermodynamic properties. Besides, for several mixtures, the /6 second constituent may be of an order higher than the "stagnation" constituent.

Following from the above, the collection of authors [2, 3, 5, 6] has demonstrated that the effect of heat of chemical reactions on heat transfer in uniform gaseous mixtures is sufficiently taken into account if, in the general relations applicable to the calculation of heat transfer without chemical reactions, we utilize so-called "effective" thermophysical and thermodynamic properties of uniform systems. Thus, Schotte [2], comparing the calculated and experimental values of thermal diffusivity of dissociative nitrogen tetroxide, N_2O_4, when P = 1 atm., came to the conclusion that the method of evaluation of thermal diffusivity of a uniform dissociative gas through "effective" thermophysical properties gives highly satisfactory results.

Based on such assumptions, a methodology for the calculation of thermodynamic functions of dissociative systems has been developed.

In the present work, a thermodynamic analysis is carried out on one of the most intensively studied systems of the dissociative cases -- nitrogen tetroxide, N_2O_4.

Physicochemical properties of nitrogen tetroxide. In the pure state, nitrogen tetroxide, N_2O_4 (colorless crystals), exists only at low temperatures. At temperatures above 262° K -- it is a crystal mass, slightly lemon colored; with increased temperature, a reddish borax colored liquid.

The reddish borax coloring of the nitrogen tetroxide under ordinary conditions is explained by the presence of molecules of nitric oxide in the mixture which appear by reason of the reversible equilibrium reaction:

$$N_2O_4 \rightleftarrows 2NO_2 - Q_{xp_1}.$$
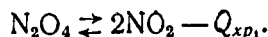
The tendency of the NO_2 (O=N=O) molecules to interact with each other is conditioned by the presence in each, when bound to an atom of nitrogen, of one unpaired (odd) electron (in a molecule of NO_2 there are 17 electrons, 5 in N_2 and 2 x 6 in O_2). Insofar as the valence bond is realized by electron pairing, a system with an even number of electrons is more stable than one of molecules containing odd electrons.

Molecules with an odd number of electrons tend toward various joint reactions, particularly toward polymerization. The combining of such unpaired electrons during polymerization creates N-N bonds in molecules of N_2O_4. The instability of N_2O_4 molecules is explained by the instability of this bond.

TABLE 1. PHYSICOCHEMICAL PROPERTIES OF NITROGEN TETROXIDE.

Quantity	Value	Reference
Molecular weight	92.02	[9]
Melting point	+262°K	[9]
	262.2°K	[10]
Boiling point at P = 1.02 atm.	294°K	[9]
	295°K	[2]
	294.5°K	[10]
Critical temperature	431°K	[9]
	431.5°K	[10]
Critical volume	165.3 cm^3/mol	[11]
Critical pressure	99 atm.	[9-11]
Surface tension at 293°K	26.5 erg/cm^2	[11]
Heat of formation N_2O_4 (gas)	+2650 cal/mol	[10]
	+2303 cal/mol	[7]
N_2O_4 (liquid)	-5210 cal/mol	[10]
Latent heat of evaporation at 294°K	9110 cal/mol	[11]
Latent heat of fusion at 283.1°K	32.2 cal/g	[10]
Standard evaporation entropy at 294°K	30.96 cal/mol	[11]
Specific weight N_2O_4 (liquid) at: 262°K	1.5124 g/cm^3	[10]
273°K	1.4905 g/cm^3	[11]

In Table 1, the basic physicochemical properties of nitrogen tetroxide are listed.

The saturated vapors above the liquid tetroxide consist of NO_2 and N_2O_4, existing in a state of dynamic equilibrium $N_2O_4 \gtrless 2NO_2$. With an increase in temperature, the dissociation $N_2O_4 \gtrless 2NO_2$ increases, and at a temperature of 430–450°K and a pressure of 1.02 atm., N_2O_4 completely goes to NO_2. In the liquid phase, the degree of dissociation is not great. In the gaseous phase, the effect of dissociation on the thermophysical properties is substantial. At more elevated temperatures (T > 450°K), dissociation of the nitrous oxide occurs
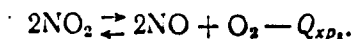
$$2NO_2 \rightleftarrows 2NO + O_2 - Q_{xp_2}.$$

The thermophysical properties of the first reaction $N_2O_4 \rightleftharpoons 2NO_2$ have been sufficiently learned for the liquid and gaseous phases [12–15], but investigation of the second stage of the reaction, $2NO_2 \rightleftharpoons 2NO + O_2$, is still insufficient [15, 16].

As is evident from the referenced list of works, the volume of experimental data is insufficient for the determination of thermodynamic properties over a wide range of temperatures and pressures. Based on this data, calculation is performed with the following assumptions: /7

1) A dissociative gas is an ideal gas, and its equation of state is

$$Pv = \frac{RT}{\mu_{N_2O_4}} (1 + \alpha_1 + \alpha_1\alpha_2),$$

where P is the total pressure of the mixture, v is the specific volume of the mixture, R is the universal gas constant and α_1, α_2 are the degrees of dissociation of the first and second stages of the reaction.

2) the equilibrium constant is independent of the pressure;

3) the reactions take place in parallel.

The calculation of enthalpy and entropy in the gaseous phase. The calculation was performed under the conditions of an equilibrium reaction. The equilibrium constants were taken from the experimental data of Bodenstein [12, 16]:
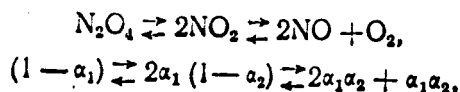
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$$\log K_{p_1} = - \frac{12310}{4,575 T} + 1,75 \log T + 4,83 \cdot 10^{-3} T - 7,144 \cdot 10^{-6} T^2 + 3,062 \tag{1}$$

in the range 290-573°K,

$$\log K_{p_2} = - \frac{5749}{T} + 1,75 \cdot \log T - 5,0 \cdot 10^{-4} T + 2,839 \tag{2}$$

in the range 400-1000°K, where K_{p_1} and K_{p_2} are the equilibrium constants of the first and second stages of the reaction.

The change in the number of mols, related to the original number of mols of N_2O_4, can be written

$$N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2,$$
$$(1 - \alpha_1) \rightleftarrows 2\alpha_1 (1 - \alpha_2) \rightleftarrows 2\alpha_1\alpha_2 + \alpha_1\alpha_2,$$

from which the total number of mols is

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$$\Sigma = (1 - \alpha_1) + 2\alpha_1 (1 - \alpha_2) + 2\alpha_1\alpha_2 + \alpha_1\alpha_2 = 1 + \alpha_1 + \alpha_1\alpha_2.$$

The instantaneous molecular weight, expressed in terms of the molecular weight of the initial composition of N_2O_4 equals

$$\mu_i = \frac{\mu_{N_2O_4}}{1 + \alpha_1 + \alpha_1\alpha_2}.$$

If we assume that the components of the mixture are ideal gases, then the equation of state for the component and for the mixture has the form:

for the first stage of the reaction

$$p_{N_2O_4} v_1 = n(1 - \alpha_1) RT,$$
$$p_{NO_2} v_1 = n 2\alpha_1 RT,$$
$$Pv_1 = n(1 + \alpha_1) RT, \tag{3}$$

or for one mole

$$p_{N_2O_4} v_1 = (1 - \alpha_1) RT,$$

$$p_{NO_2} v_1 = 2\alpha_1 RT,$$

$$Pv_1 = (1 + \alpha_1) RT,\qquad(4)$$

from which the partial pressure is

$$p_{N_2O_4} = \frac{1-\alpha_1}{1+\alpha_1} P, \quad p_{NO_2} = \frac{2\alpha_1}{(1+\alpha_1)} P,\qquad(5)$$

$$K_{p_1} = \frac{4\alpha_1^2}{1-\alpha_1^2} P,\qquad(6)$$

for the second stage of the reaction

$$p_{NO_2} = \frac{2(1-\alpha_2)}{2+\alpha_2} P, \quad p_{NO} = \frac{2\alpha_2}{2+\alpha_2} P;$$

$$p_{O_2} = \frac{\alpha_2}{2+\alpha_2} P,\qquad(7)$$

$$K_{p_2} = \frac{\alpha_2^3}{(2+\alpha_2)(1-\alpha_2)} P.\qquad(8)$$

The change in the effective entropy and enthalpy values in the chemically reactive mixture can be calculated utilizing the known thermodynamic relations of the mixture [17]:

$$dI = dU + PdV + VdP,\qquad(9)$$

$$TdS = dU + PdV.\qquad(10)$$

Transforming equations (9) and (10) and taking into consideration the properties of thermodynamic potentials (I, S) like the functions T and P, we get the following equations, suitable for calculation:

$$dI = c_p dT + \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP,\qquad(11)$$

$$dS = c_P \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP. \tag{12}$$

Integrating (11) and (12) along the isotherm between the pressure P and the infinitesimal pressure P_0, we get:

$$I - I_0 = \int_{P_0}^{P} \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP, \tag{13}$$

$$S - S_0 = -\int_{P_0}^{P} \left(\frac{\partial V}{\partial T}\right)_P dP. \tag{14}$$

Since I_0 and S_0 represent the enthalpy and entropy of ideal gases, they can be written as an additive function:

$$I_0 = x_A I_A^0 + x_B I_B^0 + \cdots + x_i I_i^0 = \Sigma x_j I_j^0, \tag{15}$$

$$S_0 = x_A S_A^0 + x_B S_B^0 + \cdots + x_i S_i^0 = \Sigma x_j S_j^0, \tag{16}$$

where x_j is the ~~smallest part~~ molal share of the component. For each separate component

$$I_j^0 = \int_{T_0}^{T} c_P \, dT + I_{0j}^0, \tag{17}$$

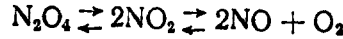$$S_j^0 = \int_{T_0}^{T} c_P \frac{dT}{T} + S_{0j}^0, \tag{18}$$

where I_{0j}^0 and S_{0j}^0 are the corresponding enthalpy and entropy values of the component, when the pure component is considered under standard conditions. From this, equations (13) and (14) can be written in the form:

$$I_{eff} = \Sigma x_j I_j^0 + \int_{P_0}^{P} \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP, \tag{19}$$

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$$S_{eff} = \Sigma x_j S_j^0 - \int_{P_0}^{P} \left(\frac{\partial V}{\partial T}\right)_P dP - R \Sigma x_i \ln x_i. \tag{20}$$

For an ̶b̶a̶l̶a̶n̶c̶e̶d̶ equilibrium system

$$N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$$

the effective enthalpy and entropy of the system, including the effect of dissociation, are equal to

$$I_{eff} = \frac{1}{\mu_{N_2O_4}} \left[I_{0\,N_2O_4}(1-\alpha_{10}) + I_{0\,NO_2} 2\alpha_{10}(1-\alpha_{20}) + I_{0\,NO} 2\alpha_{10}\alpha_{20} + \right.$$

$$\left. + I_{0\,O_2}\,\alpha_{10}\alpha_{20} \right] + \int_{P_0}^{P} V - T \left(\frac{\partial V}{\partial T}\right)_P dP, \tag{21}$$

$$S_{eff} = \frac{1}{\mu_{N_2O_4}} \left[S_{0\,N_2O_4}(1-\alpha_{10}) + S_{0\,NO_2} 2\alpha_{10}(1-\alpha_{20}) + S_{0\,NO} 2\alpha_{10}\alpha_{20} + \right.$$

$$\left. + S_{0\,O_2}\,\alpha_{10}\alpha_{20} \right] - \frac{R}{\mu_{N_2O_4}} \left[(1-\alpha_{10})\ln(1-\alpha_{10}) + 2\alpha_{10}(1-\alpha_{20})\ln 2\alpha_{10}(1-\alpha_{20}) + \right.$$

$$+ 2\alpha_{10}\alpha_{20}\ln 2\alpha_{10}\alpha_{20} + \alpha_{10}\alpha_{20}\ln\alpha_{10}\alpha_{20} - (1+\alpha_1+\alpha_1\alpha_2)\ln(1+\alpha_1+\alpha_1\alpha_2) -$$

$$\left. - \int_{P_0}^{P} \left(\frac{\partial V}{\partial T}\right)_P dP \right], \tag{22}$$

where α_{10} and α_{20} are the degrees of dissociation for the first and second stages of the reactions at pressure P_0;

$$I_{0i} = \Delta H_{0i}^{298} + i_i;$$

$$S_{0i} = \Delta S_{0i}^{298} + S_i. \tag{23}$$

Here ΔH_{0i}^{298} is the heat of formation; i_i are the components at standard conditions; ΔS_{0i}^{298} is the standard entropy.

The values for the standard heat of formation and the standard entropy are

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as follows [7]:

Component	N_2O_4	NO_2	NO	O_2
ΔH_{0i}^{298}, Kcal/g·mol	2.309	8.091	21.600	0
ΔS_{0i}^{298}, Kcal/g·mol·°	72.73	57.47	50.34	49.0

Using the equations of thermal capacity deduced by Karapet'yants [7], and integrating them, we get equations for the relative enthalpy and entropy of the component:

$$
\left.
\begin{aligned}
i_{N_2O_4} &= 20{,}05\,(T-298) + 4{,}75\cdot10^{-3}\,(T^2-298^2) + 3{,}56\cdot10^5\left(\frac{1}{T}-\frac{1}{298}\right) \\
i_{NO_2} &= 10{,}26\,(T-298) + 1{,}02\cdot10^{-3}\,(T^2-298^2) + 1{,}161\cdot10^5\left(\frac{1}{T}-\frac{1}{298}\right) \\
i_{NO} &= 7{,}03\,(T-298) + 0{,}46\cdot10^{-3}\,(T^2-298^2) + 0{,}14\cdot10^5\left(\frac{1}{T}-\frac{1}{298}\right) \\
i_{O_2} &= 8{,}64\,(T-298) + 0{,}101\cdot10^{-3}\,(T^2-298^2) + 1{,}03\cdot10^5\left(\frac{1}{T}-\frac{1}{298}\right)
\end{aligned}
\right\}
\tag{24}
$$

$$
\left.
\begin{aligned}
S_{N_2O_4} &= 20{,}05\ln\frac{T}{298} + 9{,}5\cdot10^{-3}\,(T-298) + 1{,}78\cdot10^5\left(\frac{1}{T^2}-\frac{1}{298^2}\right) \\
S_{NO_2} &= 10{,}26\ln\frac{T}{298} + 2{,}04\cdot10^{-3}\,(T-298) + 0{,}805\cdot10^5\left(\frac{1}{T^2}-\frac{1}{298^2}\right) \\
S_{NO} &= 7{,}03\ln\frac{T}{298} + 0{,}92\cdot10^{-3}\,(T-298) + 0{,}07\cdot10^5\left(\frac{1}{T^2}-\frac{1}{298^2}\right) \\
S_{O_2} &= 8{,}643\ln\frac{T}{298} + 0{,}202\cdot10^{-3}\,(T-298) + 0{,}515\cdot10^5\left(\frac{1}{T^2}-\frac{1}{298^2}\right)
\end{aligned}
\right\}
\tag{25}
$$

Following from the assumptions shown above, the specific weight can be <u>/11</u> expressed by the equation

$$
V = \frac{RT\,(1+\alpha_1+\alpha_1\alpha_2)}{\mu_{N_2O_4}\,P}.
\tag{26}
$$

Differentiating (26) at constant pressure, we get

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{\mu_{N_2O_4} P}\left[(1+\alpha_1+\alpha_1\alpha_2)+T\left(\frac{\partial\alpha_1}{\partial T}+\alpha_2\frac{\partial\alpha_1}{\partial T}+\alpha_1\frac{\partial\alpha_2}{\partial T}\right)\right].$$ (27)

Using the isobar of Vant-Hoff and the relationship of constant equilibrium, from the stages of dissociation at (6) and (8), we have:

$$\left(\frac{\partial\alpha_1}{\partial T}\right)=\frac{\Delta Q_{xp_1}}{2RT^2}\alpha_1(1-\alpha_1^2),$$ (28)

$$\left(\frac{\partial\alpha^2}{\partial T}\right)=\frac{\Delta Q_{xp_2}}{6RT^2}\alpha_2(2-\alpha_2-\alpha_2^2).$$ (29)

We can write the changes in the heats of chemical reaction, ΔQ_{xp_1} and ΔQ_{xp_2}, at the first and second stages of the reaction in the form:

$$\Delta Q_{xp_1}=2I_{NO_2}-I_{N_2O_4}=\Delta H_{p_1}+2i_{NO_2}-i_{N_2O_4},$$ (30)

$$\Delta Q_{xp_2}=2I_{NO}+I_{O_2}-2I_{NO_2}=\Delta H_{p_2}+2i_{NO}+i_{O_2}-2i_{NO_2}.$$ (31)

Solving equations (21)-(31) simultaneously, we get the desired formulas for the changes in enthalpy and entropy of the dissociative gas N_2O_4:

$$J_{eff}=\frac{1}{\mu_{N_2O_4}}[i_{N_2O_4}(1-\alpha_{10})+i_{NO_2}2\alpha_{10}(1-\alpha_{20})+i_{NO}2\alpha_{10}\alpha_{20}+i_{O_2}\alpha_{10}\alpha_{20}+$$
$$+2309+13873\alpha_{10}+27018\alpha_{10}\alpha_{20}]-$$
$$-\frac{1}{\mu_{N_2O_4}}\int_{P_0}^{P}\left[\frac{\Delta Q_{xp_1}}{2}\alpha_1(1-\alpha_1^2)(1+\alpha_2)+\frac{\Delta Q_{xp_2}}{6}\alpha_1(2+\alpha_2)(1-\alpha_2)\right]\frac{dP}{P},$$ (32)

$$S_{eff}=\frac{1}{\mu_{N_2O_4}}[S_{N_2O_4}(1-\alpha_{10})+S_{NO_2}2\alpha_{10}(1-\alpha_{20})+S_{NO}2\alpha_{10}\alpha_{20}+S_{O_2}\alpha_{10}\alpha_{20}+$$
$$+72,73+43,21\cdot\alpha_{10}+34,74\alpha_{10}\alpha_{20}]-\frac{R}{\mu_{N_2O_4}}[(1-\alpha_{10})\ln(1-\alpha_{10})+$$
$$+2\alpha_{10}\alpha_{20}\ln 2\alpha_{10}\alpha_{20}+\alpha_{10}\alpha_{20}\ln\alpha_{10}\alpha_{20}-(1+\alpha_{10}+\alpha_{10}\alpha_{20})\ln(1+\alpha_{10}+\alpha_{10}\alpha_{20})]+$$

$$+ \frac{R}{\mu_{N_2O_4}} \int_{P_0}^{P} \left[1 + \alpha_1 + \alpha_1\alpha_2 + \frac{\Delta Q_{xp_1}}{2RT} \alpha_1(1-\alpha_1^2)(1+\alpha_2) + \right.$$

$$\left. + \frac{\Delta Q_{xp_2}}{6RT} \alpha_1\alpha_2(2+\alpha_2)(1-\alpha_2) \right] \frac{dP}{P}, \quad (33)$$

where α_{10} and α_{20} represent the degree of dissociation of the first and second stages of the reaction, respectively, at P_0; α_1 and α_2 being functions of the temperature and pressure.

Based on the derived relationships, the "effective" enthalpy and entropy were computed on an electronic computer, the "Minsk-2", over a wide range of /12 temperatures and pressures (T = 300-1000°K; P = 1-130 atm.). The results of the calculations are shown in Table 2.

TABLE 2. VALUES OF "EFFECTIVE" ENTHALPIES AND
ENTROPIES DEPENDING ON TEMPERATURE AND PRESSURE.

T, K°	a. P, ama					
	1		2		5	
	b. $I_{эфф}$	$S_{эфф}$	$I_{эфф}$	$S_{эфф}$	$I_{эфф}$	$S_{эфф}$
450	212,6	1,348	210,5	1,314	206,3	1,265
500	234,2	1,393	231,1	1,358	227,3	1,310
550	264,3	1,351	257,8	1,408	250,7	1,355
600	305,9	1,523	294,4	1,472	281,6	1,408
650	360,2	1,607	342,7	1,545	323,5	1,470
700	415,2	1,692	394,4	1,627	368,4	1,543
750	469,7	1,768	448,3	1,702	419,1	1,613
800	517,1	1,830	498,2	1,767	469,4	1,679
850	554,7	1,876	538,9	1,817	513,8	1,733
900	584,7	1,910	572,4	1,855	551,4	1,776
950	609,3	1,937	599,9	1,885	583,0	1,811
1000	630,1	1,958	622,9	1,909	609,7	1,838

T, °K	P, ama							
	10		20		40		60	
	$I_{эфф}$	$S_{эфф}$	$I_{эфф}$	$S_{эфф}$	$I_{эфф}$	$S_{эфф}$	$I_{эфф}$	$S_{эфф}$
450	200,9	1,224	192,2	1,176	179,0	1,119	169,2	1,082
500	224,4	1,274	220,7	1,236	215,4	1,196	211,0	1,170
550	246,4	1,316	242,5	1,278	238,6	1,241	236,0	1,218
600	273,9	1,364	267,4	1,322	262,0	1,282	259,0	1,259
650	311,0	1,418	300,5	1,370	291,2	1,324	286,5	1,295
700	531,1	1,484	336,0	1,428	323,2	1,377	316,6	1,348
750	398,1	1,549	378,9	1,488	361,7	1,431	352,7	1,399
800	447,1	1,613	425,2	1,549	404,8	1,487	393,6	1,453
850	492,5	1,668	470,1	1,604	447,9	1,540	434,8	1,502
900	532,6	1,715	511,8	1,652	489,6	1,588	476,5	1,551
950	567,1	1,752	548,7	1,692	528,2	1,630	515,4	1,594
1000	596,7	1,783	580,9	1,725	562,6	1,666	550,9	1,630

Legend: a = P, atm.; b = I_{eff}.

TABLE 2. (Continued)

T, °K	a. P, ama					
	80		100		130	
b.	$I_{эфф}$	$S_{эфф}$	$I_{эфф}$	$S_{эфф}$	$I_{эфф}$	$S_{эфф}$
450	161,5	1,054	155,2	1,032	147,6	1,006
500	207,1	1,151	203,5	1,135	198,8	1,115
550	233,9	1,202	232,1	1,189	229,7	1,174
600	257,0	1,243	255,3	1,230	253,4	1,216
650	283,0	1,280	280,7	1,269	277,5	1,250
700	312,3	1,329	309,2	1,314	305,7	1,297
750	346,8	1,377	342,5	1,361	337,7	1,342
800	386,2	1,429	380,6	1,411	374,4	1,390
850	426,7	1,479	420,2	1,459	412,8	1,437
900	467,3	1,525	460,2	1,506	452,0	1,483
950	506,1	1,568	498,9	1,548	490,4	1,524
1000	542,1	1,605	535,2	1,585	526,8	1,562

For evaluation of the assumptions used, verifying calculations were carried out for the enthalpy and entropy in the gaseous phase through the "effective" coefficient of compressibility, developed on the basis of experimental data for P-V-T [18], in the range of pressures P = 1-130 atm. and temperatures T = 300-440°K, and at the known relationships [7]: /13

$$I_{eff} = I_0 - \int_{P_0}^{P} \left(\frac{\partial Z_{eff}}{\partial T}\right)_P \frac{RT^2}{P} dP, \tag{34}$$

$$S_{eff} = S_0 - \frac{R}{\mu_{N_2O_4}} \int_{P_0}^{P} \left[\frac{T}{P} \left(\frac{\partial Z_{eff}}{\partial T}\right)_P + \frac{Z_{eff}}{P}\right] dP. \tag{35}$$

The results of comparable calculations are shown in Table 3. These calculations are in sufficiently close agreement. The largest discrepancy constitutes an 8.5% divergence for enthalpies and a 2.9% for entropies.

The observed discrepancies can be considered fully permissible for carrying out preliminary calculations in turbomachinery, heat exchangers, and thermodynamic cycles.

TABLE 3. RESULTS OF VERIFYING CALCULATIONS OF ENTHALPY AND ENTROPY.

P	a. $I_{эфф}$ через $Z_{эфф}$	$S_{эфф}$ через $Z_{эфф}$	$I_{эфф}$	$S_{эфф}$	ΔI	ΔS	b. % ошибки	
							I	s
				350° K				
1	144,9	1,172	144,9	1,172				
3	116,2	1,053	114,5	1,048	0,7	0,005	1,47	0,47
5	101,6	0,996	100,5	0,991	1,1	0,005	1,08	0,50
				380° K				
1	180,5	1,269	180,5	1,269				
3	167,7	1,194	162,1	1,178	5,6	0,016	3,26	1,34
5	156,6	1,146	149,5	1,125	7,1	0,021	4,54	1,83
10	135,5	1,067	129,9	1,049	5,6	0,018	4,14	1,69
20	108,6	0,976	110,4	0,975	—1,8	0,001	1,67	0,10
				410° K				
1	197,3	1,312	197,3	1,312				
3	188,7	1,247	189,6	1,248	—0,9	—0,001	0,48	0,80
5	182,9	1,213	183,1	1,211	—0,2	0,002	0,11	0,16
10	172,8	1,162	170,4	1,152	2,4	0,010	1,39	0,86
20	156,6	1,097	153,1	1,084	3,5	0,013	2,24	1,19
40	129,1	1,009	133,3	1,011	— 4,2	—0,002	3,25	1,99
50	117,4	0,975	127,0	0,988	—10,0	—0,013	8,5	1,34
				420° K				
1	201,4	1,322	201,4	1,322				
3	198,0	1,270	195,5	1,262	2,5	0,008	1,26	0,63
5	195,0	1,242	190,5	1,229	4,5	0,013	2,30	1,04
10	187,9	1,196	180,3	1,176	7,6	0,020	4,10	1,67
20	174,4	1,140	165,3	1,114	9,1	0,026	5,20	2,28
40	151,5	1,062	146,6	1,044	4,9	0,018	3,23	1,69
50	140,3	1,029	140,1	1,020	0,2	0,009	0,14	0,87
60	128,2	0,996	134,9	1,002	—6,7	—0,006	5,20	0,62
				430° K				
1	205,2	1,331	205,2	1,331				
3	203,0	1,281	200,5	1,274	2,5	0,007	1,23	0,54
5	200,9	1,256	196,6	1,243	4,3	0,013	2,15	1,03
10	195,6	1,216	188,5	1,196	7,1	0,02	3,64	1,64
20	184,7	1,164	176,0	1,139	8,7	0,025	4,70	2,15
40	166,8	1,098	158,9	1,073	7,9	0,025	4,75	2,28
50	157,9	1,070	152,7	1,050	3,3	0,020	3,36	1,87
60	149,3	1,045	147,5	1,032	1,8	0,013	1,20	1,24
80	131,7	0,997	139,2	1,003	—3,5	—0,006	2,68	0,60
90	131,0	0,970	135,8	0,991	—4,8	—0,021	3,10	2,15

Legend: a = I_{eff} through Z_{eff}; b = % error.

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